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(54) Title: SUPERABSORBENT POLYMERS HAVING A SLOW RATE OF ABSORPTION

(57) Abstract: Superabsorbent polymers having a slow rate of absorption, and a process for their preparation. The superabsorbent polymer has a slow rate of absorption, is crosslinked with a covalent crosslinking agent and the metal of a polyvalent metal coordination compound, has the metal of the coordination compound distributed essentially homogeneously throughout the polymer, and has an Absorption Rate Index of at least 5 minutes. Prepare water-swellaable, water-insoluble polymer particles having a slow rate of water absorption by polymerizing a monomer in the presence of a covalent crosslinking agent and a polyvalent metal coordination compound under conditions such that there is formed a polymer having reversible cationic crosslinks and such that the metal is distributed essentially homogeneously throughout the polymer particles.

SUPERABSORBENT POLYMERS HAVING A SLOW RATE OF ABSORPTION

This invention relates to superabsorbent polymer compositions and a process for preparing said compositions.

5 Superabsorbent polymers are well-known materials which commonly are used in personal care articles such as diapers. These polymers are known to absorb several times their weight of, for example, water, saline solution, urine, blood, and serous bodily fluids.

10 The development of increasingly thinner diapers has led to diapers having a high density absorbent core, the core having an increased superabsorbent polymer fraction in the superabsorbent polymer/cellulose fluff mixture. Accordingly, the need to have homogeneous distribution of liquid in the absorbent core is increasingly important in order to fully utilize the highly swellable polymer's storage capacity. However, the distribution of liquid is negatively affected by a reduction in the amount of cellulose fluff in the absorbent core. Thus, additional requirements are now being placed on the highly swellable, liquid-
15 storing polymers in terms of liquid management. The liquid-storing polymers must allow, or support, the distribution of the liquid within the superabsorbent polymer/fluff mix, even in a superabsorbent polymer/fluff mix with a high fraction of highly swellable polymers.

In diapers having a high superabsorbent polymer/ fluff ratio, the low fluff content can result in poorer liquid distribution, since the distribution capacity of the fluff is
20 insufficient to compensate for the high absorption rate and absorption capacity of conventional superabsorbent polymers. Accordingly, a very large proportion of body fluid entering a personal care article is absorbed by the superabsorbent polymer in the immediate vicinity of the point of fluid entry.

25 The swelling of a conventional superabsorbent polymer occurs in such a way that a very high absorption rate is observed immediately after an aqueous liquid is added. After only a few minutes, a highly swellable polymer based on crosslinked, partially neutralized polyacrylate has achieved approximately 95 percent of its absorption capacity, under conditions of free swelling. This behavior is a typical property of crosslinked polyacrylate superabsorbent polymers.

30 The rapid expansion of the polymer particles around the point of entry of the body fluid into the area of the absorbent core causes a closing of the interstitial spaces and pores in the SAP-fluff matrix. Since the transport of liquid by diffusion through a swollen

hydrogel is much slower than transport through the interstitial spaces, a sealing effect occurs in the area of fluid entry. This effect is often referred to as "gel blocking." Subsequent amounts of fluid can no longer penetrate into the absorbent core and tend to flow in an uncontrolled manner across the surface of the already superficially saturated area to its edge, resulting in undesirable leakage from the absorbent core.

In addition, the storage capacity of the absorbent core decreases, since as a result of the gel blocking of the particles near the surface, the highly swellable polymers embedded deeper in the absorbent core can no longer be reached by subsequent body fluid doses, and hence can not contribute to the total storage capacity.

One approach to the gel blocking problem is to alter the absorption velocity properties of the superabsorbent polymers. For example, U.S. Patent 4,548,847 describes hydrogels reversibly crosslinked by means of at least divalent metal cations, such as Ca^{+2} or Ba^{+2} . The patent teaches that a delay in swelling can be accomplished by application of so-called "cation removal agent." Preferred examples of these are water-soluble compounds such as Na_2HPO_4 , sodium hexameta-phosphate and the disodium salt of ethylenediaminetetraacetic acid. The effect of these substances is that the reversible crosslinking sites formed by at least divalent metal cations are destroyed by the cation removal agent. With reduced crosslinking density, the product is able to swell more. The patent also describes absorbent articles that contain the absorbent polymers with the delayed swelling feature. An absorbent article built in layers (wound dressing) is described, for instance, in which each layer contains the polymers according to the invention.

GB 2,280,115 A describes an absorbent article that contains coated superabsorbent particles in the area in which body fluids are released. The coating of the superabsorbent particles prevents swelling until the coating has dissolved in the test or body fluid or has been penetrated by it. These are superabsorbent particles that exhibit an activation time until swelling begins, which time can be varied by the coating's material and thickness. Some of the coating materials disclosed are non-reactive polysaccharides such as gelatin, microcrystalline cellulose and cellulose derivatives. The activation period to the start of swelling should be at least 5, preferably 15 and more strongly preferred, 60 minutes.

Coated superabsorbent polymers have the disadvantage that even a small initial wetting, without necessarily leading to the swelling of the highly swellable polymers, leads to a destruction of the surface treatment by dissolution, detachment, swelling or

decomposition. Once the coating around the polymers has dissolved, such superabsorbent polymers exhibit the high swelling rate of a conventional material without surface treatment. Thus the desired effect of improved liquid management in the absorbent material is lost.

5 EP 0 631 768 A1 describes an absorbent article that uses superabsorbent polymers with different absorption velocities. The differences in absorption velocities between the various conventional superabsorbent polymers used arise from different particle size distributions (type 1: 600-850 μm , type 2: < 250 μm) and are correspondingly small.

The problem of gel blocking has been particularly noted in multilayer absorbent articles. One means of solving this problem has been to incorporate slow-rate
10 polymers into the articles. Several means of producing these have been suggested. However, none of these methods produce a totally satisfactory slow-rate polymer.

It would be desirable to have a process for preparing a superabsorbent polymer having a slow rate of absorption which would not require the use of a cation removing agent or a coating for the polymer. One clear advantage of such a process is the
15 cost savings associated with eliminating the use of the extra materials.

The present invention includes an improved process for the preparation of superabsorbent polymers having a slow rate of absorption, and the polymers prepared by the process. More specifically, the process is a process for the preparation of water-swella-
20 ble, water-insoluble polymer particles having a slow rate of water absorption, the process comprising polymerizing a monomer in the presence of a covalent crosslinking agent and a polyvalent metal coordination compound under conditions such that there is formed a polymer having reversible cationic crosslinks and such that the metal is distributed essentially homogeneously throughout the polymer particles. The polymer of the invention is a water-swella-
25 ble, water-insoluble polymer having a slow rate of absorption, the polymer being crosslinked with a covalent crosslinking agent and the metal of a polyvalent metal coordination compound and having the metal of the coordination compound distributed essentially homogeneously throughout the polymer, wherein the Absorption Rate Index is at least 5 minutes. In another embodiment, the present invention includes articles containing the slow rate superabsorbent polymer.

A preferred process for preparing the improved water-swellable, water-insoluble polymer of the invention involves polymerizing a suitable monomer in the presence of a covalent crosslinking agent and a polyvalent metal coordination compound.

5 The term "Absorption Rate Index" (ARI) refers to the Absorption Rate Index as measured according to the ARI Test Method described hereinbelow.

The polyvalent metal coordination compound can be any coordination compound which contains a polyvalent metal, which is at least partially soluble in the reaction mixture under reaction conditions, and which can be used to prepare a superabsorbent polymer having an Absorption Rate Index of at least five minutes. The
10 polyvalent metal coordination compound is preferably water soluble. The polyvalent metal coordination compound may be added directly as a compound, such as aluminum citrate, or may be formed *in situ* by adding precursor components such as, in the case of aluminum citrate, for example, an aluminum salt, such as aluminum sulfate, and a source of the desired ligand, such as, in the case of aluminum citrate, for example, citric acid. Preferably, the
15 metal cation has a valence of at least +3, with Al being most preferred. Examples of preferred ligands in the polyvalent metal coordination compound include citrates, oxylates, lactates, glycinate, ethylenediaminetetraacetic acid, and acetates, with citrates being most preferred. Aluminum citrate is the most preferred polyvalent metal coordination compound and is readily commercially available. Mixtures of polyvalent metal coordination compounds
20 or their precursors can be employed. In a preferred embodiment, the coordination compound is essentially free of divalent metal ions.

In the present invention, a polyvalent metal coordination compound suitably is employed in an amount sufficient to produce a polymer having an Absorption Rate Index which is at least 5 minutes. Preferably, at least 0.003 mole of metal ion of the polyvalent
25 metal coordination compound is employed per mole of carboxyl moieties on the substrate polymer. More preferably, at least 0.016 mole of metal ion of the polyvalent metal coordination compound, and most preferably at least 0.03 mole of metal ion of the polyvalent metal coordination compound is employed per mole of carboxyl moieties on the substrate polymer. Preferably, no more than 0.1 mole of metal ion of the polyvalent metal
30 coordination compound is employed; more preferably, no more than 0.086 mole of metal ion

of the polyvalent metal coordination compound is employed; and most preferably, no more than 0.07 mole of metal ion of the polyvalent metal coordination compound is employed per mole of carboxyl moieties on the substrate polymer. Preferably, the amount of metal ion of the polyvalent metal coordination compound employed is from 0.003 to 0.1 mole, more
5 preferably from 0.016 to 0.086 mole; and most preferably from 0.03 to 0.07 mole per mole of carboxyl moieties on the substrate polymer.

The preferred process of the invention involves polymerizing a suitable monomer in the presence of a covalent crosslinking agent and a polyvalent metal coordination compound.

10 The water-swellaable or lightly crosslinked hydrophilic polymers suitably employable in the present invention can be any of the known hydrophilic polymers which are capable of absorbing large quantities of fluids. In particular, water-absorbent polymers useful in this invention are water-absorbent polymers which contain carboxyl moieties. Preferably, at least 0.01 equivalent of carboxyl groups are present per 100 grams of the
15 water-absorbent resin.

Among preferred carboxyl-containing water absorbent polymers are hydrolyzates of starch-acrylonitrile graft copolymers, partially neutralized products of starch-acrylic acid or polyvinyl alcohol graft copolymers, saponification products of vinyl acetate acrylic ester copolymers, derivatives of copolymers of isobutylene and maleic
20 anhydride, hydrolyzates of acrylonitrile copolymers, crosslinked products of hydrolyzates of acrylonitrile copolymers, crosslinked carboxymethyl cellulose, polyaspartate hydrolyzates of acrylamide copolymers, crosslinked products of hydrolyzates of acrylamide copolymers, partially neutralized products of polyacrylic acids and crosslinked products of partially neutralized polyacrylic acids.

25 Examples of some suitable water-swellaable, water-insoluble polymers and processes, including gel polymerization processes, for preparing them are disclosed in U.S. Patent Numbers 3,997,484; 3,926,891; 3,935,099; 4,090,013; 4,093,776; 4,340,706; 4,446,261; 4,683,274; 4,459,396; 4,708,997; 4,076,663; 4,190,562; 4,286,082; 4,857,610; 4,985,518; and 5,145,906. In addition, see Buchholz, F.L. and Graham, A.T., "Modern
30 Superabsorbent Polymer Technology," John Wiley & Sons (1998). Such hydrophilic

polymers are prepared from water-soluble α,β -ethylenically unsaturated monomers such as monocarboxylic acids, polycarboxylic acids, acrylamide and their derivatives.

Suitable α,β -ethylenically unsaturated monomers include, for example, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid and alkali metal salts and ammonium salts thereof; itaconic acid, acrylamide, methacrylamide and 2-acrylamido-2-methyl-1-propane sulfonic acid and its salts. The preferred monomers include acrylic acid and methacrylic acid and their respective salt forms such as alkali metal or ammonium salts. The water-soluble monomers useful in the present invention may be used in amounts ranging from 10 percent to 80 percent by weight based on the total weight of the aqueous monomer solution. Preferably, the amount ranges from 15 percent to 60 percent based on the total weight of the aqueous monomer solution.

Optionally, minor amounts of other water-soluble, unsaturated monomers, such as alkyl esters of the acid monomers, for example, methyl acrylate or methyl methacrylate may be present in the water absorbent polymer. In addition, certain grafting polymers, such as, for example, polyvinyl alcohol, starch and water soluble or swellable cellulose ethers may be employed to prepare products having superior properties. Such grafting polymers, when employed, are used in amounts up to 10 weight percent based on the α,β -ethylenically unsaturated monomer.

The polymerization may be carried out using acid monomers that are not neutralized or that have been neutralized or partially neutralized prior to the polymerization. Neutralization is conveniently achieved by contacting the aqueous monomer with an amount of basic material sufficient to neutralize between 20 and 95 percent of the acid groups present in the acid monomers. Preferably, the amount of basic material will be sufficient to neutralize between 40 percent and 85 percent, and most preferably between 55 percent and 75 percent of the acid groups present in the acid monomers.

Compounds which are useful to neutralize the acid groups of the monomer are typically those which will sufficiently neutralize the acid groups without having a detrimental effect on the polymerization process. Examples of such compounds include alkali metal hydroxides, and alkali metal carbonates and bicarbonates. Preferably, sodium or potassium hydroxides or carbonates are employed to neutralize the monomer. In

determining the desired degree of neutralization, care must be taken to ensure that the pH of the resulting crosslinked absorbent polymer, which will be contacted with or dispersed in an aqueous fluid to be absorbed, is maintained in a range appropriate for the applications for which the polymer is intended. Alternatively, the polymerization may be carried out
5 employing unneutralized monomers and thereafter neutralizing, as is known in the art.

Conveniently, a conventional vinyl addition polymerization initiator is used in the polymerization of the water-soluble monomers and the crosslinking agent. A free radical polymerization initiator which is sufficiently soluble in the monomer solution to initiate polymerization is preferred. For example, water soluble persulfates such as potassium
10 persulfate, ammonium persulfate, sodium persulfate, and other alkali-metal persulfates, hydrogen peroxide and water soluble azo-compounds such as 2,2'-azobis-(2-amidinopropane) hydrochloride may be used. Some of these initiators, such as hydrogen peroxide, can be combined with reducing substances such as sulfites or amines to form known redox type initiators. The total amount of initiators used may range from 0.01 to 1.0
15 weight percent, preferably 0.01 to 0.5 weight percent, based on the total weight of α,β -ethylenically unsaturated monomer reactants.

The water-absorbent resin will preferably be lightly covalently crosslinked to render it water-insoluble and water-swellaable. The desired crosslinked structure may be obtained by the copolymerization of the selected water-soluble monomer and a crosslinking
20 agent possessing at least two polymerizable double bonds in the molecular unit. The crosslinking agent is present in an amount effective to covalently crosslink the water-soluble polymer. The preferred amount of crosslinking agent is determined by the desired degree of absorption capacity and the desired strength to retain the absorbed fluid, that is, the desired absorption under load (AUL). Typically, the crosslinking agent is used in amounts ranging
25 from 0.0005 to 5 parts by weight per 100 parts by weight of α,β -ethylenically unsaturated monomer used. More preferably, the amount ranges from 0.1 to 1 part by weight per 100 parts by weight of the α,β -ethylenically unsaturated monomer. Usually, if an amount over 5 parts by weight of crosslinking agent per 100 parts monomer is used, the resulting polymer has too high a crosslinking density and exhibits a reduced absorption capacity and increased
30 strength to retain the absorbed fluid. If the crosslinking agent is used in an amount less than 0.0005 part by weight per 100 parts monomer, the polymer usually has too low a

crosslinking density, and when contacted with the fluid to be absorbed becomes sticky and exhibits a lower initial absorption rate.

While the covalent crosslinking agent will typically be soluble in the aqueous solution of the α,β -ethylenically unsaturated monomer, the crosslinking agent may be merely dispersible in such a solution without negative implications. The use of such dispersing agents is disclosed in U.S. Patent 4,833,222, the teachings of which are incorporated herein by reference. Suitable dispersing agents include carboxymethyl cellulose suspending aids, methyl cellulose, hydroxypropyl cellulose, and polyvinyl alcohol. Such dispersing agents are typically provided at a concentration between 0.005 and 0.1 weight percent, based on the total weight of α,β -ethylenically unsaturated monomer reactants.

Typical covalent crosslinking agents include monomers having in one molecule 2 to 4 groups selected from the group consisting of $\text{CH}_2=\text{CHCO}-$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}-$ and $\text{CH}_2=\text{CH}-\text{CH}_2-$. Exemplary covalent crosslinking agents include: diacrylates and dimethacrylates of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, trimethylolpropane and pentaerythritol; triacrylates and trimethacrylates of trimethylolpropane and pentaerythritol; highly ethoxylated trimethylol propane triacrylate; tetracrylate and tetramethacrylate of pentaerythritol; allyl methacrylate; and tetraallyloxyethane. Mixtures of covalent crosslinking agents can be employed.

In a preferred embodiment for making polymers useful in the practice of this invention, an aqueous solution of the α,β -ethylenically unsaturated monomer in the partially neutralized form, the covalent crosslinking agent, the polyvalent metal coordination compound, the initiator and a grafting polymer substrate, if desired, is prepared. The polymerization of the mixture may be initiated by elevating the temperature of the mixture containing the initiator or by using a redox-type initiator as described above. Generally, the temperature at which polymerization will begin ranges from 5°C to 45°C. The temperature at which the polymerization is carried out is highly dependent on the type of monomers used and the specific initiator system employed. Preferably, the maximum temperature of polymerization ranges from 50°C to 100°C, most preferably from 60°C to 100°C.

The resultant polymer is typically pre-sized and dried using means well-known in the art. Suitable drying means include fluidized bed driers, rotary driers, forced air ovens and through-circulation band dryers. In some instances, drying will occur in two or more stages, that is, multi-stage drying. Following the completion of drying, the polymer is further sized to form particles preferably having an average diameter less than 2 mm and more preferably less than 1 mm. Preferably, the final polymer product has an average particle size of at least 160 microns.

To further decrease the rate of absorption, the dried particles may be heat treated in accordance with the procedures set forth in WO 93/05080, and/or U.S. 5,629,377. Such heat treatment is preferably carried out at a temperature of at least 170°C, more preferably of at least 180°C, and most preferably of at least 190°C. Such heat treatment is preferably carried out at a temperature of less than 250°C, more preferably less than 240°C. The method of heat treatment is not critical. For example, forced air ovens, fluidized bed heaters, heated screw conveyors, may be successfully employed. If desired, the heated polymer may be remoisturized for ease in handling.

A way to improve absorptive properties of the polymer particles may be to surface crosslink the polymer particles. Procedures for surface crosslinking are well known in the art and described in, for example, U.S. 4,734,478 and U.S. 4,666,983. These procedures may increase the modulus and/or the absorbency under load of the polymer particles.

The composition of the invention can optionally include other additives such as, for example, anticaking agents. Anticaking agents are well-known. Silica is an example of a preferred anticaking agent.

The composition of the invention exhibits a slow rate of absorbency. Preferably, the composition has an Absorption Rate Index of at least 5 minutes, more preferably at least 10 minutes, even more preferably at least 20 minutes and most preferably at least 30 minutes.

The superabsorbent polymers of this invention are useful in the manufacture of moisture absorbent articles, such as disposable diapers, sanitary napkins, incontinence

garments and bandages. The superabsorbent compositions of this invention are particularly useful in the manufacture of thin and ultra thin disposable diapers which have excellent moisture absorbence capacity, fluid distribution properties and reduced leakage. For example, the superabsorbent polymers of this invention can be used in the manufacture of absorbent articles such as those described in U.S. Patent Numbers 3,669,103; 3,670,731; 4,654,039; 4,430,086; 4,973,325; 4,892,598; 4,798,603; 4,500,315; 4,596,567; 4,676,784; 4,938,756; 4,537,590; 4,673,402; 5,061,259; 5,147,343; and 5,149,335. Construction of diapers and other absorbent articles is well known, and materials useful as fluff in absorbent articles are also well known. For the purposes of the present invention, the term "fluff" is given its meaning as understood by those of ordinary skill in the art. Examples of fluff include cotton fibers, curly fibers, wood pulp fibers, synthetic fibers, or a combination thereof, which are formed into a pad and absorb primarily by capillary attraction mechanism. See, for example, U.S. Patent 4,610,678.

In making absorbent articles with the compositions of this invention, the superabsorbent composition may be mixed with, attached to, layered in, or dispersed in a porous matrix of fibers. Such matrices are made with hydrophilic fibers such as wood pulp or fluff, cotton linters, and synthetic fibers or a mixture of the fibers and the wood fluff. The fibers can be loose or joined as in nonwovens. Examples of synthetic fibers include those made using polyethylene, polypropylene, polyesters, and copolymers of polyesters and polyamides. The synthetic fibers may be meltblown fibers or fibers which have been treated to render them hydrophilic.

The superabsorbent polymers of this invention are even more advantageously utilized in absorbent structures that incorporate superabsorbent polymers having a slow absorption rate, either alone or in tandem with superabsorbent polymers having different absorption rates, in multi-compartmentalized or multi-layered structures. Examples of such structures are described in U.S. Patent Numbers 4,338,371; 4,935,022; 5,364,382; 5,429,629; 5,486,166; 5,520,673; 5,531,728; 5,562,646; and 5,728,082.

The superabsorbent polymers of this invention are also advantageously used in those manufacturing processes where contact with aqueous fluids is inherent to the process. In these processes, slow absorption rate helps to prevent excessive superabsorbent

swelling, which swelling results in large amounts of water to be removed and large volume changes occurring upon drying. Examples of such processes are wet-laid composite processes, and processes for making foam absorbent structures. Examples of wet-laid composite processes are described in U.S. Patent Numbers 4,354,901; 4,986,882; 5,300,192; 5,308,896; 5,538,783; 5,543,215; 5,795,439 and 5,651,862. Examples of foam absorbent structures are described in U.S. Patent Numbers 4,990,541 and 5,011,864.

Absorbent articles, such as disposable diapers, typically are made with a liquid-impermeable backing material, a liquid-permeable bodyside facing material and the liquid-absorbing composite sandwiched between the backing material and the facing material. The liquid-impermeable backing material can be made from commercially available polyolefin film and the liquid-permeable facing material can be made from a commercially available nonwoven material, such as spunbonded or corded fibrous web which is wettable and capable of passing urine.

The absorbent articles of the invention may comprise from 5 percent to 95 percent by weight of the superabsorbent polymers of the invention. In a typical absorbent article, the superabsorbent polymer of the invention can be dispersed in a fiber matrix; in such an article the superabsorbent advantageously is present in an amount from 30 to 70 weight percent based on the weight of the article and the fiber matrix is present in an amount of from 70 to 30 weight percent based on the weight of the article. In another form of absorbent article, the superabsorbent may be present in a containment structure in which the superabsorbent polymer is present in an amount of 30 to 95 percent by weight. Combinations of dispersed superabsorbent polymer and contained superabsorbent polymer are also known.

The following examples and comparative experiments are given to illustrate the invention and should not be construed as limiting its scope. All parts and percentages are by weight unless otherwise indicated.

The absorption capacity (AC) is measured according to the method stated in Buchholz, F.L. and Graham, A.T., "Modern Superabsorbent Polymer Technology," John Wiley & Sons (1998), page 153.

Homogeneous distribution of the metal of the metal salt of the invention in the superabsorbent polymer is measured according to the electron microprobe analysis method as described at Buchholz, F.L. and Graham, A.T., *id.* at pages 57-58.

ARI Test Method: Method for Determination of the Absorption Rate Index

5 A 100 mL graduated cylinder is filled with 100 mL of 0.9 wt percent aqueous saline solution. A superabsorbent polymer sample is screened to -30/+50 mesh using ASTM-E-11 specification screens. A 1.00 g portion of the screened polymer is dumped into the graduated cylinder. When the sample first reaches the bottom of the graduated cylinder, a timer accurate to the nearest second is started. The volume of the gel layer is measured at
10 times of 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 15, 30, 60, 90, 180, 330 and 480 minutes. The data is plotted and the time required for the gel volume to reach 60 percent of its value at 8 hours is determined by interpolation. This time is reported as the t60 time, and for the purposes of the present invention is the "Absorption Rate Index."

Example 1:

15 Preparation of the aluminum citrate complex:

Into a 200 mL beaker containing 45.6 g deionized water was dissolved 10.20 g citric acid (Aldrich Chemical). To this was added 35.4 g aluminum sulfate 14 hydrate (General Chemical). The mixture was stirred for 5 minutes.

Preparation of the monomer solution:

20 A solution of 169.14 g of sodium carbonate in deionized water was prepared in a 1 L beaker. In a 2 L beaker was placed 353.49 g glacial acrylic acid. To this was added 1.77 g highly ethoxylated trimethylol propane triacrylate (HeTMPTA)(SARTOMER #9035, Sartomer). A 276.8 g portion of deionized water was then added followed by 0.44 g
25 VERSENEX 80 (The Dow Chemical Company). The carbonate solution was then slowly added from an addition funnel. The solution of aluminum sulfate and citric acid was then added.

Polymerization:

The monomer mix was placed in a 2 L jacketed resin kettle equipped with an agitator rotating at 30 RPM. The jacket temperature was set to 30°C and nitrogen was sparged through the solution at a rate of 750 sccm to deoxygenate the monomer mix. After one hour of deoxygenation, 0.12 g 30 wt percent hydrogen peroxide was added followed by 5.66 g 10 wt percent sodium persulfate. The polymerization began immediately. The temperature rose to 78°C in 8 minutes, then the kettle was cooled to keep its temperature below 86°C. As the exotherm subsided, the jacket temperature was set to 65°C and held there for three hours.

10 Drying and sizing:

The reaction mass was in the form of crumbs. Those pieces larger than about 2.5 cm were removed, and 300 g of the remainder was dried at 165°C for 30 min. The dried product was ground in a roll mill and was then screened to -20/+120 mesh using ASTM E-11 specification screens.

15 The two hour AC of the sample was 26.0 g/g. The swelling rate of the sample was characterized using the ARI Test Method, and the Absorption Rate Index was determined to be 12 minutes.

Comparative Experiment A

20 The procedure of Example 1 was repeated except that no aluminum citrate complex was employed. Polymerization initiation required the addition of 0.53 g sodium erythorbate after the addition of the persulfate. This sample had a two-hour AC of 31.3 g/g and an Absorption Rate Index of 2½ minutes.

Examples 2-16

25 The procedure of Example 1 was repeated with variations as shown in Table I and except that the aluminum sulfate was a 50 wt percent solution of iron-free grade available from General Alum and Chemical Corporation. The samples were also heat-treated at various temperatures for an additional ½ hour. The 8 hour capacity in Table I was defined

as: $0.6 * (\text{gel volume at 8 hr}) - 1.7$, wherein the gel volume was measured according to the ARI Test Method defined hereinabove.

Table I: Results of Examples 2-16

| Example Number | HeTMPA (g) | 50 Percent Aluminum Sulfate (g) | Citric Acid (g) | Heat-treatment Temperature (deg C) | 8 Hour Capacity (g/g) | Absorption Rate Index (min) |
|----------------|------------|---------------------------------|-----------------|------------------------------------|-----------------------|-----------------------------|
| 2 | 1.06 | 88.50 | 19.13 | 185 | 28.6 | 27.7 |
| 3 | 1.06 | 88.50 | 19.13 | 185 | 28.3 | 25.8 |
| 4 | 1.77 | 70.80 | 15.30 | 185 | 26.8 | 17.5 |
| 5 | 1.06 | 88.50 | 19.13 | 185 | 28.6 | 28.7 |
| 6 | 1.06 | 70.80 | 15.30 | 175 | 33.3 | 22.4 |
| 7 | 1.77 | 88.50 | 19.13 | 175 | 26.5 | 23.1 |
| 8 | 1.06 | 106.20 | 22.95 | 195 | 26.0 | 45.7 |
| 9 | 0.35 | 70.80 | 15.30 | 185 | 41.5 | 30.7 |
| 10 | 1.06 | 106.20 | 22.95 | 175 | 26.5 | 39.3 |
| 11 | 1.06 | 70.80 | 15.30 | 195 | 31.8 | 24.0 |
| 12 | 1.77 | 106.20 | 22.95 | 185 | 22.1 | 26.0 |
| 13 | 0.35 | 106.20 | 22.95 | 185 | 31.8 | 49.8 |
| 14 | 0.35 | 88.50 | 19.13 | 195 | 39.5 | 48.3 |
| 15 | 1.77 | 88.50 | 19.13 | 195 | 24.8 | 24.3 |
| 16 | 0.35 | 88.50 | 19.13 | 175 | 37.7 | 44.3 |

CLAIMS:

1. A process for the preparation of water-swella-
ble, water-insoluble polymer particles having a slow rate of water absorption, the process comprising
polymerizing a monomer, in the presence of a covalent crosslinking agent and a polyvalent
metal coordination compound, under conditions such that there is formed a polymer having
covalent crosslinks and reversible cationic crosslinks and such that the metal is distributed
essentially homogeneously throughout the polymer particles, the particles having an
Absorption Rate Index of at least 5 minutes.
2. The process of Claim 1 wherein the Absorption Rate Index is at least
10 minutes.
3. The process of Claim 1 wherein the absorption rate index is at least 20
minutes.
4. The process of Claim 1 wherein the absorption rate index is at least 30
minutes.
5. The process of Claim 1 wherein the polymer is selected from the
group consisting essentially of the hydrolyzates of starch-acrylonitrile graft copolymers,
partially neutralized products of starch-acrylic acid or starch-polyvinyl alcohol graft
copolymers, saponification products of vinyl acetate acrylic ester copolymers, derivatives of
copolymers of isobutylene and maleic anhydride, hydrolyzates of acrylonitrile
carboxymethyl cellulose, hydrolyzates of acrylamide copolymers, and partially neutralized
products of polyacrylic acids.
6. The process of Claim 1 wherein the polymer is partially neutralized
polyacrylic acid.
7. The process of Claim 1 wherein the metal cation of the polyvalent
metal coordination compound has a valence of at least +3.
8. The process of Claim 1 wherein the metal cation of the polyvalent
metal coordination compound is aluminum.

9. The process of Claim 1 wherein the ligand of the polyvalent metal coordination compound is citrate.

10. A polymer prepared by the process of Claim 1.

11. An absorbent article comprising the composition of Claim 1.

5 12. The article of Claim 11 which is a diaper or part of a diaper wherein the weight ratio of superabsorbent polymer composition to fluff is at least 0.3.

10 13. A process for the preparation of water-swellaable, water-insoluble polymer particles having a slow rate of water absorption, the process comprising polymerizing an ethylenically unsaturated monomer selected from the group consisting of a carboxylic acid or the esters, vinyl amine, amides, salts thereof, or a mixture thereof, in the presence of a covalent crosslinking agent and a polyvalent metal coordination compound wherein the metal is aluminum, under conditions such that there is formed a polymer having reversible cationic crosslinks and such that the metal is distributed essentially homogeneously throughout the polymer particles.

15 14. The process of Claim 13 wherein the ligand of the coordination compound is citrate.

15. The process of Claim 13 wherein the monomer is a partially neutralized carboxylic acid.

20 16. The process of Claim 13 wherein the coordination compound is aluminum citrate.

17. A polymer prepared by the process of Claim 13.

25 18. A process for the preparation of water-swellaable, water-insoluble polymer particles having a slow rate of water absorption, the process comprising polymerizing a monomer comprising partially neutralized acrylic acid in the presence of a covalent crosslinking agent, an aluminum salt and citric acid under conditions such that there is formed a polymer having covalent crosslinks and reversible cationic crosslinks and such

that the aluminum of the aluminum salt is distributed essentially homogeneously throughout the polymer particles.

19. A water-insoluble, water-swellaable polymer having an Absorption Rate Index of at least 5 minutes, wherein the polymer is covalently crosslinked, contains a homogeneous distribution of a metal from a polyvalent metal coordination compound, and is reversibly cationically crosslinked.
20. The polymer of Claim 19 wherein the metal is aluminum.
21. The polymer of Claim 19 wherein the Absorption Rate Index is at least 10 minutes.
22. The polymer of Claim 19 wherein the Absorption Rate Index is at least 20 minutes.
23. An absorbent article comprising the composition of Claim 19.
24. The article of Claim 23 which is a diaper or part of a diaper wherein the weight ratio of superabsorbent polymer composition to fluff is at least 0.3.

INTERNATIONAL SEARCH REPORT

Int. Appl. No.
PCT/US 00/31487

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61L15/00 B01J20/26 C08F8/32 C08F220/06 C08F265/04
C08F251/00 C08L51/00 C08L51/02 C08K5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61L A61F C08F B01J C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------------------|
| X | US 4 954 562 A (ANDERSON MARK) 4 September 1990 (1990-09-04) | 1-8, 10-13, 15,17, 19-24 |
| Y | * claims 38,39,43,1,6,9,10 ; column 8, line 42-48 ; column 7, line 3 - column 9, line 29 ; column 11, line 55 - column 12, line 17 * column 13, line 10 -column 15, line 52; examples 1-33 --- -/-- | 9,14,16, 18 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

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P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Int. Appl. Application No
PCT/US 00/31487

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|---|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | <p>US 5 629 377 A (BURGERT JOSEF H ET AL) 13 May 1997 (1997-05-13)</p> <p>* claim 9 + column 36, line 11-12 ; claims 10-20 ; claim 1 + column 3, line 53-54 ; claims 2,8 ; column 4, line 58 - column 7, line 64 ; column 13, line 44 - column 14, line 23 * column 12, line 46 -column 13, line 43</p> <p style="text-align: center;">---</p> | <p>1-6, 10-12, 19,21-24</p> |
| Y | <p>EP 0 040 763 A (MILES LAB) 2 December 1981 (1981-12-02) page 3, line 13-28</p> <p style="text-align: center;">---</p> | <p>9,14,16, 18</p> |
| Y | <p>US 5 744 564 A (STANLEY JR DECEASED FREDERICK ET AL) 28 April 1998 (1998-04-28)</p> <p>* example 1 ; column 4, line 53 - column 6, line 6 * column 8, line 67</p> <p style="text-align: center;">---</p> | <p>1-8, 10-13, 15,17, 19-24</p> |
| Y | <p>WO 96 05234 A (UMADA AKIRA ;AMIYA TAKAYUKI (JP); KAO CORP (JP); NAMBU HIROMI (JP)) 22 February 1996 (1996-02-22)</p> <p>* page 14, line 19 ; page 16, line 15 * page 13, line 22 -page 18, line 16</p> <p style="text-align: center;">---</p> | <p>1-8, 10-13, 15,17, 19-24</p> |
| Y | <p>US 4 548 847 A (RING GERARD J F ET AL) 22 October 1985 (1985-10-22) cited in the application</p> <p>* claims 16,17,1-15,18,19 ; figures 1-8 * abstract</p> <p style="text-align: center;">---</p> | <p>1-8, 10-13, 15,17, 19-24</p> |
| Y | <p>US 5 447 727 A (GRAHAM ANDREW T) 5 September 1995 (1995-09-05)</p> <p>* example 1 * claims 1-25</p> <p style="text-align: center;">---</p> | <p>1-8, 10-13, 15,17, 19-24</p> |
| A | <p>EP 0 316 518 A (VER PAPIERWERKE AG) 24 May 1989 (1989-05-24) * claim 4 * abstract</p> <p style="text-align: center;">---</p> | <p>9,14,16, 18</p> |
| A | <p>WO 95 00183 A (MOELNLYCKE AB ;WIDLUND URBAN (SE); GUIDOTTI EDWARD (SE); OESTERDAH) 5 January 1995 (1995-01-05) cited in the application abstract; claims 1-7</p> <p style="text-align: center;">-----</p> | <p>1-24</p> |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/31487

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|---|--|
| US 4954562 A | 04-09-1990 | US 4677174 A US 4755562 A AT 56456 T CA 1268295 A DE 3674197 D EP 0242478 A US 4820773 A US 4985518 A AT 81137 T CA 1276370 A DE 3686884 A DE 3686884 T EP 0248963 A MX 167235 B US 4824901 A | 30-06-1987 05-07-1988 15-09-1990 24-04-1990 18-10-1990 28-10-1987 11-04-1989 15-01-1991 15-10-1992 13-11-1990 05-11-1992 25-02-1993 16-12-1987 11-03-1993 25-04-1989 |
| US 5629377 A | 13-05-1997 | DE 69405217 D DE 69405217 T EP 0688340 A JP 8510484 T WO 9420547 A | 02-10-1997 19-03-1998 27-12-1995 05-11-1996 15-09-1994 |
| EP 0040763 A | 02-12-1981 | AU 7102081 A CA 1137510 A DE 3160844 D DK 230881 A,B, FI 811602 A,B, MX 155240 A NO 811619 A,B, PH 17645 A US 4447364 A | 10-12-1981 14-12-1982 13-10-1983 28-11-1981 28-11-1981 09-02-1988 30-11-1981 18-10-1984 08-05-1984 |
| US 5744564 A | 28-04-1998 | WO 9319099 A AT 165751 T AU 1752292 A DE 69225354 D DE 69225354 T EP 0516925 A JP 6506252 T MX 9201201 A WO 9216565 A | 30-09-1993 15-05-1998 21-10-1992 10-06-1998 03-12-1998 09-12-1992 14-07-1994 01-10-1992 01-10-1992 |
| WO 9605234 A | 22-02-1996 | JP 3118779 B JP 8053550 A JP 2938775 B JP 8176311 A DE 69505398 D DE 69505398 T EP 0775161 A ES 2123278 T US 5883158 A | 18-12-2000 27-02-1996 25-08-1999 09-07-1996 19-11-1998 11-03-1999 28-05-1997 01-01-1999 16-03-1999 |
| US 4548847 A | 22-10-1985 | AU 3739085 A BR 8500094 A EP 0149998 A JP 60227755 A ZA 8500053 A | 18-07-1985 13-08-1985 31-07-1985 13-11-1985 28-08-1985 |

INTERNATIONAL SEARCH REPORT

information on patent family members

Int. onal Application No
PCT/US 00/31487

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|---|--|
| US 5447727 A | 05-09-1995 | AU 5329994 A BR 9307292 A EP 0664816 A JP 8506363 T WO 9409043 A | 09-05-1994 01-06-1999 02-08-1995 09-07-1996 28-04-1994 |
| EP 0316518 A | 24-05-1989 | DE 3738601 A AT 119381 T ES 2070120 T | 24-05-1989 15-03-1995 01-06-1995 |
| WO 9500183 A | 05-01-1995 | SE 501699 C AT 192658 T AU 677677 B AU 7087694 A CA 2165089 A CZ 9503351 A DE 69424422 D DE 69424422 T EP 0706402 A ES 2148334 T FI 956092 A GB 2280115 A GR 3033722 T HU 76080 A,B JP 8511459 T NO 955194 A NZ 268118 A PL 312291 A PT 706402 T SE 9302146 A SK 157495 A US 5855571 A ZA 9404252 A | 24-04-1995 15-05-2000 01-05-1997 17-01-1995 05-01-1995 17-04-1996 15-06-2000 26-10-2000 17-04-1996 16-10-2000 18-12-1995 25-01-1995 31-10-2000 30-06-1997 03-12-1996 13-02-1996 24-10-1997 15-04-1996 29-09-2000 22-12-1994 03-07-1996 05-01-1999 08-02-1995 |